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REPORT DOCUMENTATI

AD-A266 786

IRPOSES
pproved
o 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	May 93	Final 26 Feb 90-15 Feb 93

4. TITLE AND SUBTITLE

Structural and Dynamical Aspects of Electrodeposition

5. FUNDING NUMBERS

DAAL03-90-G-0048

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

ARO 27502.4-CH

11. SUPPLEMENTARY NOTES

The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

12b. DISTRIBUTION CODE

93-15525

6pp

93 7 08 107

13. ABSTRACT (Maximum 200 words)

The final report contains a brief summary of research findings:

The basic aim of this contract was to investigate structural and dynamical aspects of electrochemical phase formation. In these investigations researchers have emphasized the underpotential deposition of metal mono and multilayers employing electrochemical, x-ray based and ultra high vacuum surface spectroscopic techniques.

They have been able to study:

1. The underpotential deposition of silver on a Pt(111)electrode as function of

   a. concentration
   b. potential sweep rate
   c. the presence of co-adsorbates

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14. SUBJECT TERMS	15. NUMBER OF PAGES
Electrodeposition, Electrochemical Phase Formation, Electrodes, Silver, Copper, Platinum	4
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

From these studies it was possible to determine that two monolayers of silver are deposited at underpotentials and that the stability of the second layer is a strong function of the concentration of silver in solution and the potential sweep rate. The presence of co-adsorbates can have a profound influence in the deposition and the magnitude of this effect(s) is strongly dependent on the type of adsorbate employed.

2. The underpotential deposition of copper on an iodine covered platinum surface by x-ray based techniques with emphasis on:

    a. isotherms derived from electrochemical and x-ray based measurements
    b. mode of deposition
    c. structure of the copper layer

Researchers have found that isotherms derived from x-ray based measurements consistently yield a significantly higher coverage (relative to electrochemically derived isotherms) that they ascribe to copper species weakly associated with the interface. The deposition appears to obey a mechanism where sites deeper in the platinum surface are occupied first and that sites further up are the progressively occupied. The structure of the copper appears to be strongly influenced by the chemisorbed iodine. The copper atoms appear to occupy bridge sites on the surface.

Final Report for ARO Proposal No. 27502-CH
Contract No. DAAL03-90-G-0048

Structural and Dynamical Aspects of Electrodeposition

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A. Brief Summary of Research Findings:

The basic aim of this contract was to investigate structural and dynamical aspects of electrochemical phase formation. In these investigations we have emphasized the underpotential deposition of metal mono and multilayers employing electrochemical, x-ray based and ultra high vacuum surface spectroscopic techniques.

We have been able to study:

1.The underpotential deposition of silver on a Pt(111) electrode as function of

a. concentration

b. potential sweep rate

c. the presence of co-adsorbates

From these studies we have been able to determine that two monolayers of silver are deposited at underpotentials and that the stability of the second layer is a strong function of the concentration of silver in solution and the potential sweep rate. The presence of co-adsorbates can have a profound influence in the deposition and the magnitude of this effect(s) is strongly dependent on the type of adsorbate employed.

2.The underpotential deposition of copper on an iodine covered platinum surface by x-ray based techniques with emphasis on:

a. isotherms derived from electrochemical and x-ray based measurements

b. mode of deposition

c. structure of the copper layer

We have found that isotherms derived from x-ray based measurements consistently yield a significantly higher coverage (relative to electrochemically derived isotherms) that we ascribe to copper species weakly associated with the interface. We have also found that the deposition appears to obey a mechanism where sites deeper in the platinum surface are occupied first and that sites further up are the progressively occupied. The structure of the copper appears to be strongly influenced by the chemisorbed iodine. The copper atoms appear to occupy bridge sites on the surface.

B. Publications acknowledging support by the Army Research Office

1. H. D. Abruña; "X-ray Absorption Spectroscopy in the Study of Electrochemical Systems" in: Electrochemical Interfaces: Modern Techniques for In-Situ Interface Characterization, H. D. Abruña, Ed. VCH Publishers, Deerfield , Florida, 1991 p.1

2. H. D. Abruña; "Probing Electrochemical Interfaces with X-rays" Advances in Chemical Physics I. Prigogine and S. A. Rice, eds. Vol. 77; Chapter 5., pp. 255-335, John Wiley & Sons, Inc. New York, N.Y. 1990

3. G. M. Bommarito, D. Acevedo and H. D. Abruña; "In-situ Monitoring of Electrochemically Induced Roughening with the Crystal Truncation Rod Technique" J. Phys. Chem. 96, 3416, (1992)

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6. Abruña, H.D.; Bommarito, G.M.; Acevedo, D.A.; "Probing Solid/Liquid Interfaces with X-ray Standing Waves"; Science 250, 69 (1990)

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9. Abruña, H. D.; "Estudios de Interfases Sólido/Líquido Utilizando Ondas Estacionarias de Rayos X" Investigación y Ciencia (Scientific American in Spanish) (invited and submitted)

10. Bommarito, G. M.; Acevedo, D.; Rodríguez, J. F.; Abruña, H. D. "In-Situ Structural Studies of the Underpotential Deposition of Copper onto an Iodine Covered Platinum Surface Using X-Ray Standing Waves" in X Rays in Materials Analysis II: Novel Applications and Recent Developments; D. M. Mills, ed. SPIE Proceedings Vol. 1550, 156-170 1991.

11. Bommarito, G. M.; Acevedo, D.; Rodríguez, J. F.; Abruña, H. D.; "In-Situ X-Ray Standing Wave Study of Cu UPD on an Iodine Covered Platinum Surface" in"Symposium on X-ray Methods in Electrochemistry" Gordon, J. G.; Davenport, A. eds. The Electrochemical Society, Pennigton, N.J. 1992 p. 125

12. Bommarito, G. M.; Acevedo, D. ; Rodríguez, J. F.; Abruña, H. D.; "In-Situ X-Ray Standing Wave Study of Cu UPD on an Iodine Treated Platinum Surface" In: Proc. Workshop on Structural Effects in Electrocatalysis and Oxygen

Electrochemistry, D. Scherson, M. Daroux, D. Tryk, X. Xing, Eds. The Electrochemical Society Inc. Pennington, N.J. 1992

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C. Individuals supported by the ARO Contract:

1. David Acevedo Ph.D. 1991
2. Mark Bommarito Ph.D. 1992
3. Dr. José F. Rodríguez
4. Donna Taylor
5. Howell Yee